OBSERVATIONS ON THE RARE EARTHS: 8-QUINOLINOL AND SUBSTITUTED 8-QUINOLINOL CHELATES OF CERTAIN RARE EARTH ELEMENTS

BY

DALE EDWARD JACKSON

A.B., University of Illinois, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

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I. Introduction

In recent years, several publications have dealt with the preparation of the compounds formed between oxine (8-quinolinol) and various rare earth elements (2,7,8,9). The resulting chelates have been proposed for use as materials suitable for the gravimetric or volumetric (6) determination of the rare earth elements. Attempts to prepare these compounds in this laboratory (3) according to the directions found in the literature have been generally unsuccessful.

These studies were undertaken, therefore, with the intent of preparing oxine derivatives of some of the rare earth elements and examining their chemical and physical properties. Although anhydrous lanthanum oxinates with definite compositions were finally prepared, a long series of failures with oxine directed attention to its 5,7-dichloro derivative. When it was found that the new reagent could be so employed as to prepare chloroform solutions of the neodymium-dichloroxine chelate, the purpose of these studies was altered to include an investigation of the absorption spectra of such solutions and the conditions essential to the successful extraction of certain rare earths into chloroform in the form of such chelates.

Inasmuch as the researches described herein dealt with certain chelated inner-complexes of the rare earth elements, and since there is no available summary on that general subject, a comprehensive review of the characteristics of rare earth inner-complexes is included.

Materials and Apparatus

The rare earth materials used in this investigation were of the maximum obtainable purity. They were drawn from the

stocks of the Division of Inorganic Chemistry at the University of Illinois. All other chemicals were of analytical-reagent grade and were used without further purification.

Two precision instruments were used: (1) the Beckman Model DU Quartz Spectrophotometer, which was employed with (generally) 5 cm., quartz window demountable cells, and (2) the Beckman Model G *p*H Meter, the glass electrode of which was calibrated frequently against standard buffer solutions.

II. Studies on Solid 8-Quinolinol and 5,7-Dichloro-8-quinolinol Chelates of Certain Rare Earth Elements

Oxinates (8-quinolinol chelates) are precipitated when a mixture of oxine and the cation in question is either formed at or brought up to approximately the *p*H at which precipitation of the hydroxide takes place. The heat-accelerated decomposition of urea in aqueous media can be used to effect a gradual rise of the *p*H of those media; therefore, several rare earth-oxine mixtures were precipitated by boiling their aqueous solutions in the presence of urea. Analyses of the dried, yellow powders by quantitative bromination and ignition showed them to have oxine contents generally insufficient for the theoretical composition, $RE(C_9H_6ON)_3$. Other approaches were used, but with negative results, until a lanthanum chloride solution was treated with an excess of oxine, and the mixture was precipitated at room temperature by the slow, dropwise addition of dilute ammonia. The resulting materials were greenish yellow and flocculent in appearance but turned dark, olive green when brought to constant weight by drying at 130°. Ignition analyses showed the lanthanum contents to have been within one per cent of theoretical.

Similar difficulties were experienced with the dichloroxinates; however, by precipitating a near-boiling mixture of neodymium chloride and dichloroxine with dilute ammonia, two precipitates were obtained which gave analyses agreeing

with the composition, $Nd(C_9H_4ONCl_2)_3$.

No accurate melting or decomposition temperatures for these substances could be obtained. Qualitative tests have shown them to be only partially soluble, (i.e.) with apparent decomposition, in several non-polar liquids.

III. Studies on Chloroform Solutions of 8-Quinolinol and Substituted 8-Quinolinol Chelates of Certain Rare Earth Elements

Two procedures were found applicable to the preparation of chloroform solutions of dichloroxine chelates of the rare earth elements; (1) a *liquid-liquid* method (first used) in which an alkaline solution of the particular lanthanon, well-buffered with ammonium acetate, is shaken with a 0.02*M* solution of dichloroxine in chloroform and (2) a *precipitation* method (the more easily handled) in which a mixture of the cation and dichloroxine is precipitated with dilute ammonia, digested for a short period, and extracted into chloroform. Neither of these methods could be used to prepare chloroform solutions of the oxine chelates which contained in excess of 0.0002 mole /l of rare earth metal.

Regardless of the cation present, complexes of this type, at least in chloroform solution, exhibit absorption in the form of a very broad peak near 4000 A. However, certain peaks of a few of the lanthanons undergo resolution, intensification, and displacement of their wave lengths. Nearly all of the rare earth ions should have peaks which are affected by complexing. However, the intense 4000 A peak of the complex itself prevents detection of any peaks, due to the rare earth ion, below 5000 A. This condition limited these studies to the chelates of neodymium, holmium, erbium, thulium, and ytterbium; and of these the first and third were investigated.

The 5745 A peak of neodymium has been found to be enhanced to about ten times its value in aqueous solution, to be divided into three bands, and to be shifted to about 5818 A.

The 5220 A absorption of erbium is shifted to 5208 A and is roughly fifteen times higher. Both of the new bands have been shown to obey Beer's Law at concentrations up to at least 0.0007 *M* for neodymium and 0.0014 *M* for erbium.

Solutions of neodymium and erbium at various *p*H values have been studied to determine the relative amounts of each element which may be extracted into chloroform as its dichloroxine chelate. These studies have shown appreciable extraction to take place at or above the *p*H values necessary for precipitation of the respective hydroxides. The basicity difference between the two elements is reflected by the incidence of erbium extraction at *p*H 5 and of neodymium at *p*H 6.2.

The magnified absorptions of these materials suggested their use in the determination of amounts of neodymium, etc., too small to be detected by absorption in aqueous solution. Accordingly the neodymium contents in four rare earth mixtures were determined spectrophotometrically (in sufficient concentration) in aqueous solution and at much lower concentrations as the dichloroxine chelates in chloroform. The respective data agreed very well.

IV. Summary

Stoichiometric lanthanum oxinates have been prepared and analyzed. However, the thermal instabilities of the rare earth chelates with oxine and dichloroxine, when formed in the presence of water, can be taken as additional evidence for the slight tendencies of the lanthanons to form chelate compounds. These tendencies are confirmed by the necessity of using large excesses of dichloroxine when the rare earth chelates of that reagent are extracted into chloroform solution. However, two extraction procedures suitable for the determination of semimicro amounts of neodymium have been developed. The *p*H-dependence of these procedures suggests their application to separative problems. The method is limited to lanthanons of widely varying basicities, however, since chelate formation

seems to reduce the already slight basicity differences between adjacent rare earth elements (10).

V. Appendix

Dichloroxine is commercially unavailable. Syntheses have been reported (1,4,5,), but attempts to repeat the most promising of these, chlorination in cold, glacial acetic acid, have given indifferent success.

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VITA

The author was born on March 10, 1923, in Decatur Illinois. He attended the public schools of that city until his graduation from high school in June, 1940.

Upon graduation from high school he was awarded, by competitive examination, a four year general scholarship to the University of Illinois. He was admitted to that institution in September, 1940, as a freshman in the Curriculm of Chemistry.

After completing three years at Illinois, which included basic and advanced R.O.T.C. courses, he was called to active duty on June 18, 1943, as a sergeant in the Coast Artillery. After eight months training he was attached to a unit at the University of Illinois and allowed to continue his studies. He received the degree of Bachelor of Arts in June, 1944.

The author was relieved from active duty as a First Lieutenant, Infantry Reserve, on October 15, 1946, after service in the Zone of the Interior and in the Pacific Theater of Operations. At that time he entered the (then) Graduate School at the University of Illinois and accepted a position as a half time assistant, teaching in chemistry. In September, 1948, he was appointed as a half time research assistant under Navy Contract N6-ori-71, T.O. VII. This appointment continued through August, 1950.

The author is a member of the American Chemical Society, Alpha Chi Sigma, Sigma Xi and Phi Lambda Upsilon. He is a joint author of the following publication:

Moeller, T. and Jackson, D. E., "Separative Extraction of Certain Rare Earth Elements as 5,7-Dichloro-8-quinolinol Chelates," Anal. Chem., 22, (1950).